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Organotin(IV) Derivatives of N-Maleoylamino Acids: Their Synthesis and Structural Elucidation

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Organotin carboxylates of general formula R_3SnL **(1), (2), (4)** and **(6)**, R_2SnL_2 **(5)** and $\{[(R_2SnL)_2O]_2\}$ **(3)**, where L = N-maleoylglycinate, N-maleoyl-β-alaninate and N-maleoylmethioninate, were prepared. The synthesis of these compounds was achieved by either reaction of organotin halides, R_3SnCl, with triethylammonium salt of N-maleoylamino acids or/and organotin oxides, $(R_3Sn)_2O$ and R_2SnO, with maleamic acid in the presence of triethyl amine. These compounds were characterized by FT-IR, multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn), mass and ^{119m}Sn Mössbauer spectroscopy. The geometry around the tin atom is compared both in solution and in solid state. Different literature methods were employed to calculate the C-Sn-C angle in non-coordinating solvents. The mass fragmentation pattern demonstrated the McLafferty rearrangement in compound **(6)**. Salient features of the X-ray structures for **(1), (4)** and **(6)** are also given.

Key Words: Organotin(IV) complexes, N-Maleoylamino acids, FT-IR, Multinuclear NMR, Mössbauer spectroscopy, Mass spectrometry.

Introduction

Organotin(IV) compounds of the carboxylic acids, especially amino acids and peptides, are being extensively studied with special reference to their methods of synthesis, structural elucidation and biological activity [1–7]. Generally these compounds are well characterized by multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn), X-ray and ^{119m}Sn Mössbauer spectroscopy [8–10]. As a continuation of our series on the synthesis and characterization of organotin carboxylates [11–23], we report here the synthesis and spectral characterization of organotin(IV) derivatives of 3 different N-maleoylamino acids (Scheme 1). The carboxylic acids used in the present work are N-maleoylglycine, N-maleoyl-β-alanine and N-maleoylmethionine. The X-ray structures of **(1)**, **(4)** and **(6)** are already published elsewhere [19–21].

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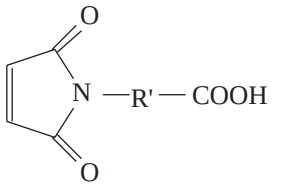


R' = CH_2 (N-maleoylglycinate)
R' = CH_2CH_2 (N-maleoyl-b-alaninate)
R' = $CH(CH_2CH_2SCH_3)$
(N-maleoylmethioninate)

Scheme 1

Experimental

All syntheses and preparative work were carried out under an inert atmosphere of argon. The glassware used was carefully dried and all solvents were dried prior to use by reported methods [24].

Instrumentation

NMR spectra were recorded using an ARX 250 instrument equipped with multinuclear units. If not mentioned otherwise, samples dissolved in $CDCl_3$ (10-20%) in 5 mm (o.d.) tubes were measured at 25 ± 1 °C. Chemical shifts are given with respect to solvent signals [(δ^1H($CHCl_3$)) = 7.24; (δ^{13}C($CDCl_3$)) = 77.0)], and external references δ^{119}Sn (Me_4Sn) = 0, Ξ (^{119}Sn) = 37.290665 MHz). Chemical shifts are given in ppm and coupling constants J are given in Hz. The multiplicities of signals in ^{1}H NMR are given with chemical shifts (s singlet, d doublet, t triplet, q quartet, m multiplet).

^{119m}Sn Mössbaurer spectra were obtained with a constant acceleration microprocessor controlled spectrometer (Cryoscopic Ltd., Oxford, UK); a barium stannate source was used at room temperature, and samples were packed in Perspex disks and cooled to 77 K. Isomer shift data are relative to SnO_2.

The FT-IR spectra of the compounds in KBr pellets were measured on a Perkin Elmer Spectrum 1000 FT-IR spectrometer. Mass spectral data were measured on a MAT 8500 Finnigan 70 eV mass spectrometer (Germany).

Synthesis

Two different methods, from organotin halides and from organotin oxides, were used for the synthesis of the reported compounds.

Synthesis from organotin halides

General procedure

N-Maleoylamino acid was prepared by stirring equimoles of maleic anhydride (0.425 mol) and amino acid (0.425 mol) in acetic acid for 3 h at room temperature [25]. The solid, maleamic acid, was filtered, washed with cold water and air-dried. Maleamic acid (8.4 mmol) was suspended in dry toluene and treated with triethylamine (17 mmol). The mixture was refluxed under vigorous stirring for 4 h. The water formed was continuously removed via a Dean-Stark apparatus. After cooling, toluene was removed from the orange layer, triorganotin chlorides (8.4 mmol) was added to the toluene and the mixture was refluxed for 3-4 h. On cooling, triethylammonium chloride was filtered off, toluene removed using rotary evaporator, and the mass left was recrystallized from either dichloromethane or a dichloromethane/n-hexane (1:1) mixture [19,21].

R = Me **(1)**, Yield: 84%, mp, 175-177 °C

IR (cm^{-1}): ν_{Asym}(COO) 1592, ν_{sym}(COO) 1424, $\Delta\nu$ = 168, ν(Sn-C) 552, ν(Sn-O) 466.

MS (m/z): $[Me_3SnOC(O)CH_2C_4H_2NO_2]^+$ M^+ (2), $[Me_2SnOC(O)CH_2C_4H_2NO_2]^+$ (100), $[Me_3Sn]^+$ (75), $[Sn/SnH]^+$ (5).

^{1}H NMR: ($CDCl_3$): 0.45 (s, 9H, $SnMe_3$) $^2J(^{119}Sn,^1H)$ (61.0), 3.04 (s, 2H, CH_2), 6.61 (s, 2H, CH=CH).

R = ^{n}Bu **(2)**, Yield: 80%, mp, 61-63 °C

IR (cm^{-1}): ν_{Asym}(COO) 1584, ν_{sym}(COO) 1424, $\Delta\nu$ = 160, ν(Sn-C) 552, ν(Sn-O) 468.

MS (m/z): $[Bu_3SnOC(O)CH_2C_4H_2NO_2]^+$ M^+ (5), $[Bu_2SnOC(O)CH_2C_4H_2NO_2]^+$ (60), $[Bu_3Sn]^+$ (85), $[BuSn]^+$ (100), $[Sn/SnH]^+$ (5).

^{1}H NMR: ($CDCl_3$): 0.88 (t, 9H, (CH_3)Bu), 1.25 (m, 6H, (CH_2)Bu), 1.34 (m, 6H, (CH_2)Bu), 1.57 (m, 6H, (CH_2)Bu), 3.09 (s, 2H, CH_2), 6.67 (s, 2H, CH=CH).

R = Me **(6)**, Yield: 72%, mp, 95-97 °C

IR (cm^{-1}): ν_{Asym}(COO) 1590, ν_{sym}(COO) 1426, $\Delta\nu$ = 164, ν(Sn-C) 548, ν(Sn-O) 460.

MS (m/z): $[Me_3SnOC(O)CH(CH_2CH_2SCH_3)C_4H_2NO_2]^+M^+$(5),

$[Me_2SnOC(O)CH(CH_2CH_2SCH_3)C_4H_2NO_2]^+$ (60), $[Me_3Sn]^+$ (100), $[Sn/SnH]^+$ (10).

^{1}H NMR: ($CDCl_3$): 0.50 (s, 9H, $SnMe_3$) $^2J(^{119}Sn,^1H)$ (59.6), 1.23 (t, 2H, CH_2-S), 2.01 (s, 3H, CH_3-S), 2.44 (m, 2H, CH_2), 3.11 (m, 1H, CH), 6.65 (s, 2H, CH=CH).

Synthesis from organotin oxides

General Procedure

Two equivalents of maleamic acid, prepared by reacting the amino acid and maleic anhydride in 1:1 ratio as described above [25], 2 equivalents of Et_3N and 1 equivalent of either $(Bu_3Sn)_2O$ or Bu_2SnO were mixed in toluene. The mixture was refluxed under stirring for 4 h. The water formed was continuously removed via a Dean-Stark apparatus. After cooling, the solvent was removed and the resulting solid material was recrystallized from either dichloromethane or a dichloromethane/n-hexane (1:1) mixture [20].

R = ^{n}Bu **(3)**, Yield: 72%, mp, 121-123 °C

IR (cm^{-1}): ν_{Asym}(COO) 1584, ν_{sym}(COO) 1420, $\Delta\nu$ = 164, ν(Sn-O-Sn) 634, ν(Sn-C) 552, 530, ν(Sn-O) 460.

MS (m/z): $\{[Bu_2SnOC(O)CH_2C_4H_2NO_2]_2O\}_2^+$ M^+ (n.o),

$[Bu_2SnOC(O)CH_2C_4H_2NO_2]^+$ (100), $[Bu_2Sn]^+$ (5), $[Sn/SnH]^+$ (2).

^{1}H NMR: ($CDCl_3$): 3.91 (s, 2H, CH_2), 6.65 (s, 2H, CH=CH), various overlapping multiplets for butyl groups.

R = ^{n}Bu **(4)**, Yield: 81%, mp, 70-72 °C

IR (cm^{-1}): ν_{Asym}(COO) 1576, ν_{sym}(COO) 1409, $\Delta\nu$ = 165, ν(Sn-C) 540, ν(Sn-O) 454.

MS (m/z): $[Bu_3SnOC(O)CH_2CH_2C_4H_2NO_2]^+$ M^+ (n.o),

$[Bu_2SnOC(O)CH_2CH_2C_4H_2NO_2]^+$ (100), $[Bu_3Sn]^+$ (5), $[Sn/SnH]^+$ (5).

^{1}H NMR: ($CDCl_3$): 0.89 (t, 9H, (CH_3)Bu), 1.26 (m, 6H, (CH_2)Bu), 1.33 (m, 6H, (CH_2)Bu), 1.57 (m, 6H, (CH_2)Bu), 2.58 (t, 2H, CH_2), 3.77 (t, 2H, CH_2), 6.66 (s, 2H, CH=CH).

R = ^{n}Bu **(5)**, Yield: 80%, mp, 77-79 °C

IR (cm^{-1}): ν_{Asym}(COO) 1580, ν_{sym}(COO) 1416, $\Delta\nu$ = 166, ν(Sn-C) 538, ν(Sn-O) 448.

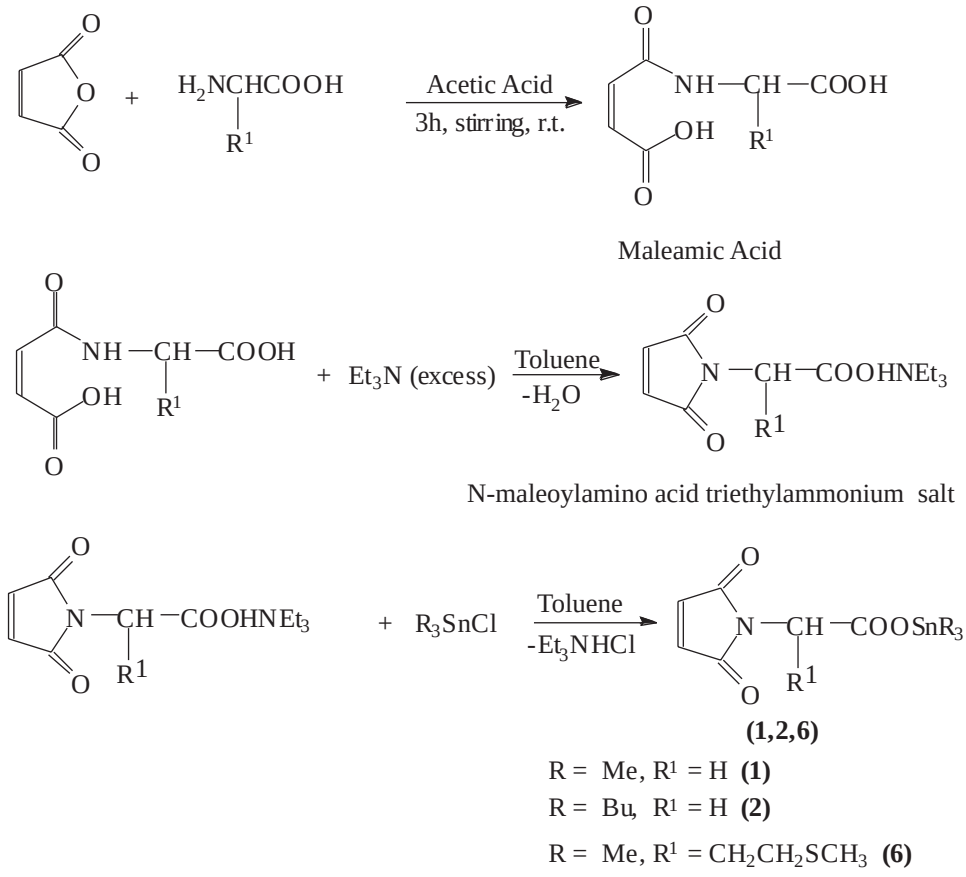
MS (m/z): $\{Bu_2Sn[OC(O)CH_2CH_2C_4H_2NO_2]_2\}^+$ M^+ (n.o),

$\{BuSn[OC(O)CH_2CH_2C_4H_2NO_2]_2\}^+$ (100), $[Bu_2Sn]^+$ (10), $[Sn/SnH]^+$ (2).

^{1}H NMR: ($CDCl_3$): 0.80 (t, 6H, (CH_3)Bu), 1.20 (m, 4H, (CH_2)Bu), 1.29 (m, 4H, (CH_2)Bu), 1.52 (m, 4H, (CH_2)Bu), 2.56 (t, 2H, CH_2), 3.71 (t, 2H, CH_2), 6.60 (s, 2H, CH=CH).

Results and Discussion

The synthesis of organotin compounds **(1), (2)** and **(6)** was achieved in 3 steps as shown in Scheme 2. Maleic anhydride when reacted with amino acids gave maleamic acid in quantitative yield [25]. The maleamic acid was then further treated with Et_3N to yield the triethylammonium salt of the maleoylamino acids. In the third step, an equimolar amount of R_3SnCl was added. After removing the solvent, the resulting solid materials were recrystallized in suitable solvents [19,21].

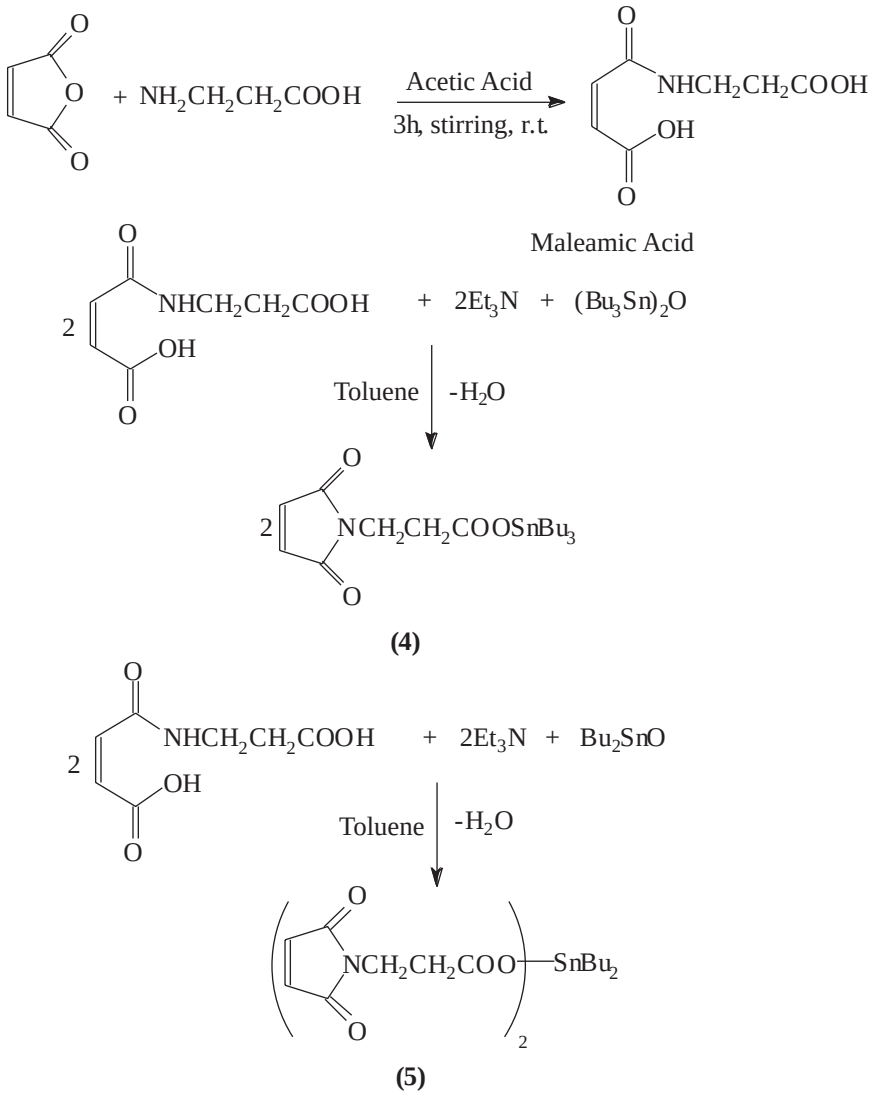


Scheme 2

The synthesis of **(4)** and **(5)** follows 2 steps. In the first step, maleic anhydride reacted with amino acids to give the corresponding maleamic acid. The second step involved the reaction of 2 equivalents of maleamic acid, 2 equivalents of Et_3N and 1 equivalent of corresponding $(R_3Sn)_2O$ or R_2SnO, where R = Bu (Scheme 3) [20].

In an attempt to prepare diorganotin dicarboxylate with the general formula $(R^1CH_2COO)_2SnBu_2$, only the compound $\{[(R^1CH_2COO)SnBu_2]_2O\}_2$ **(3)**, where $R^1 = C_4H_2NO_2$, was isolated after recrystallization as evident from the observed 2 ^{119}Sn NMR resonances of almost equal intensity (Figure 1). Apparently, either only one equivalent of acid can be consumed or the diorganotin dicarboxylates formed can undergo hydrolysis to yield the dimeric distannoxanes (Scheme 4) [26].

These synthesized compounds are solids, having sharp melting points and are soluble in common organic solvents. These newly synthesized compounds were characterized by multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) and ^{119m}Sn Mössbauer spectroscopy. X-ray analysis data for **(1)**, **(4)** and **(6)** are reported elsewhere [19–21].

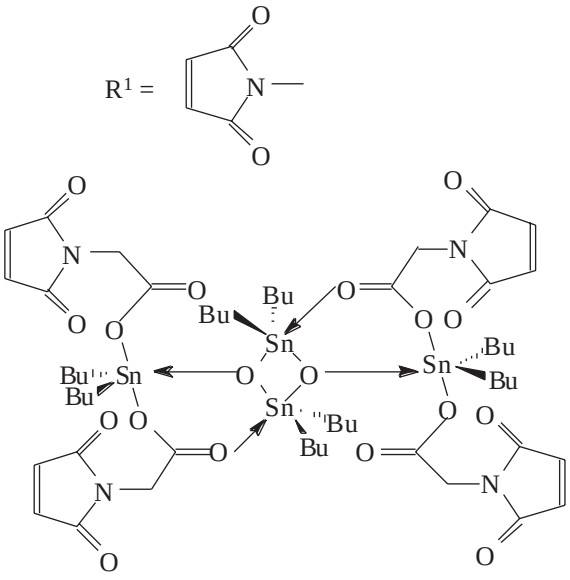


Scheme 3

$$4R^1CH_2COOH + 4Bu_2SnO \longrightarrow \{[(R^1CH_2COO)SnBu_2]_2O\}_2 + 2H_2O$$

$$4(R^1CH_2COO)_2SnBu_2 + 2H_2O \xrightarrow{-4R^1CH_2COOH} \{[(R^1CH_2COO)SnBu_2]_2O\}_2$$

(3)



(3)

Scheme 4

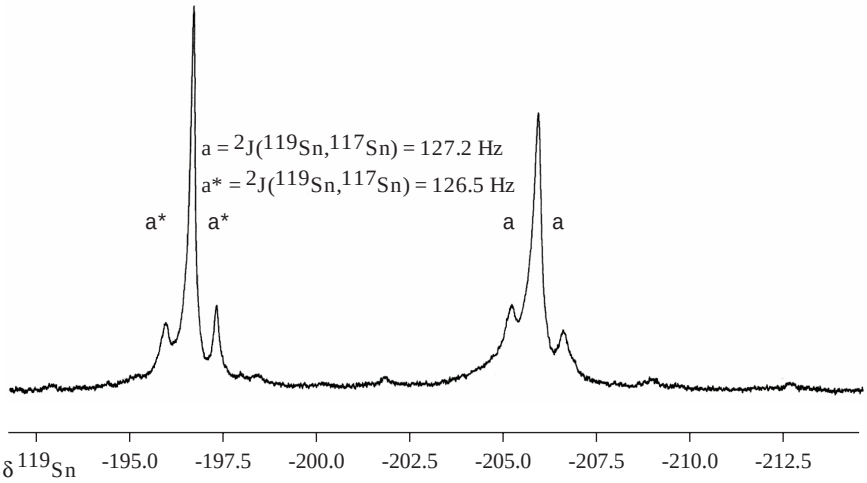


Figure. 93.3 MHz ^{119}Sn NMR spectrum of (3) in $CDCl_3$.

FT-IR Spectroscopy

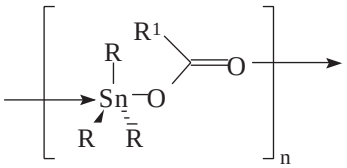
Important FT-IR data for the title compounds are given along with their synthesis in the experimental section. Absorptions in the range 530-560 and 440-470 cm^{-1} are assigned to Sn-C and Sn-O stretching vibrations respectively. The $\Delta\nu$ [$\Delta\nu = \nu(COO)_{as}$-$\nu(COO)_s$] is very useful in drawing the nature of the bonding of the carboxylates group to tin(IV) [27]. The coordination number of tin affects the absorption vibration frequency of the carbonyl group. It is generally thought that the difference $\Delta\nu$ below 200 cm^{-1}

suggests the 5 coordinated structure of triorganotin carboxylates [27] (see structure A). From the FT-IR data given in the experimental section, we can see the value of $\Delta\nu$ less than 200 cm^{-1}, suggesting that all triorganotin carboxylates are 5 coordinated owing to the bidentate or bridging nature of the carboxylate. The carbonyl absorption of diorganotin carboxylates is apparently more complicated than those of triorganotin carboxylates, because there are 2 carbonyl groups. Therefore, if the 2 carbonyl groups have the same coordination to tin, there is only 1 absorption band in the carbonyl range, but if the 2 carbonyl groups have different absorption bands then they have different coordinations to tin [27]. Since only 1 carbonyl absorption band is observed in the case of compound **(5),** a similar bidentate nature of the ligand proposes the structure **B**. The IR spectrum of compound **(3)** (dimeric dicarboxylatotetraorganodistannoxane) is similar to that of compound **(5)**, except for a very sharp band at 634 cm^{-1}, characteristics for a Sn-O-Sn-O ring in this compound [28].

Mössbauer spectroscopy

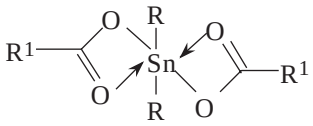
Mössbauer spectroscopy provides useful information on the geometry around the tin atom in the solid state and also to compare with their structures in solution (NMR) [29–31]. In particular, quadrupole splitting (QS) values often allow discrimination between tetrahedral, trigonal bipyramidal and *cis* or *trans* octahedral arrangements, each of them being identified by a characteristic value range (tetrahedral: 2.1-2.4 mm/s, trigonal bipyramidal: 3.0-4.1 mm/s, *cis*-octahedral: 1.7-2.2 mm/s, *trans*-octahedral: 3.5-4.2 mm/s) [31].

Table 1 lists the ^{119m}Sn Mössbauer parameters along with ^{119}Sn NMR data for these compounds. Various reports show that QS parameters fall in the range 2.30-2.55 mm/s for monomeric triorganotin carboxylates having trigonal bipyramidal geometry and a chelating carboxylate group, while those having a 5 coordinate structure formed by bridging carboxylate groups give QS parameters in the range 3.55-3.70 mm/s [31]. For compounds **(2), (4)** and **(6)** a single doublet is observed, revealing the occurrence of only 1 type of tin atom in the solid state. The QS parameters in the range 3.57–3.65 mm/s are consistent with a *trans*-R_3SnO_2 arrangement with bridging carboxylate for the triorganotin compounds **(2), (4)** and **(6)**, as shown below (Structure **A**).



A

For diorganotin dicarboxylates, the ρ value (QS/IS) plays an important role in the predication of the geometry around the tin atom. As reported earlier, if the ρ value is greater than 2.1, the diorganotin dicarboxylates possess a *trans*-octahedral geometry around the tin atom [31]. Hence, a ρ value of 2.50 mm/s strongly suggests *trans*-octahedral geometry around tin for compound **(5)**, as shown in **B** [31].



B

Table 1. ^{119m}Sn Mössbauer parameters and ^{119}Sn NMR data for the investigated compounds [a].

Comp. No. ↓	IS	QS	ρ = QS/IS	^{119}Sn[b]
(1)	-	-	-	127.0
(2)	1.41	3.65	2.59	135.2
(3)	1.29	3.50	2.71	-196.6 -205.8 [127.2]
(4)	1.39	3.57	2.57	116.1
(5)	1.35	3.37	2.50	-133.6
(6)	1.29	3.58	2.77	144.8

[a] IS = isomer shift (mm/s), QS = quadrupole splitting (mm/s)
[b] In $CDCl_3$, $^2J(^{119}\text{Sn-O-}^{119}\text{Sn})$ coupling constant in Hertz is given in [].

Mössbauer spectroscopy usually does not distinguish between the 2 different environments of tin atoms in dimeric distannoxanes [26,29−31]. This is not unexpected since Mössbauer spectroscopy has a small isomer shift range and is, therefore, less sensitive to small variations in tin environment; consequently only 1 doublet is observed. In the present case the QS value fully supports the proposed structure for compound **(3)** [26].

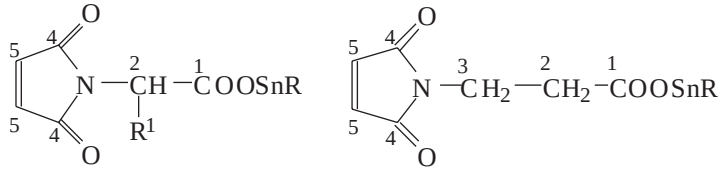
Multinuclear NMR spectroscopy

^{1}H NMR data for compounds **(1-6)** are given along with their synthesis in the experimental part. The expected resonances are assigned by their multiplicity and intensity pattern. For the trimethyltin derivatives **(1)** and **(6)**, the $^2J(^{119}\text{Sn},^1\text{H})$ are 61.0 and 59.6 Hz, which fall in the range of the tetrahedral environment around the tin atom [32]. In the case of butyl derivatives, the $^nJ(^{119}\text{Sn},^1\text{H})$ couplings are not visible due to a complex multiple pattern. Table 2 presents the ^{13}C NMR data for the organotin compounds and their ^{119}Sn NMR data are given in Table 1. The magnitudes for $^nJ(^{119}\text{Sn},^{13}\text{C})$ couplings are also observed and are given in Table 2. For triorganotin compounds **(1), (2), (4)** and **(6)**, the magnitudes of $^1J(^{119}\text{Sn},^{13}\text{C})$ couplings suggest the typical tetrahedral geometry around tin in solution [32−35]. As far as geometry of the diorganotin dicarboxylate, **(5)**, in non-coordinated solvents is concerned, it is not defined with certainty due to the fluxional behavior of the carboxylate oxygens in their coordination with the tin atom [36]. However, earlier reports suggest a geometry between penta- and hexa-coordination [32]. Various literature methods were applied to calculate the C-Sn-C bond angles in solution based on $^2J(^{119}\text{Sn},^1\text{H})$ and $^1J(^{119}\text{Sn},^{13}\text{C})$ coupling constants (Table 3) [37−39]. For the α, β and γ carbons of the butyl moieties, compound **(3)** shows pairs of ^{13}C resonances with very similar chemical shifts, the resulting overlapping precluding the observation of $^nJ(^{119}\text{Sn},^{13}\text{C})$ satellites for the β and γ carbons [26].

Table 2. ^{13}C NMR data for the investigated compounds [a–d].

Comp. No. → Carbon No. ↓	**(1)**	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**
C1	170.2	169.9	169.9	170.3	170.2	170.5
C2	39.3	39.1	40.0	33.4	32.6	51.8
C3	-	-	-	34.3	33.8	-
C4	171.8	171.4	172.5	175.6	180.4	173.5
C5	134.4	134.2	134.3	134.0	134.1	134.2
α	-2.2 [424.0]	16.7 [350.6]	29.5, 27.7 [724.9], [678.9] [678.9]	16.3 [355.9]	25.1 [567.0]	-1.9 [402.0]
β	-	27.5 [21.3]	27.4, 27.0	27.6 [20.0]	26.4 [34.3]	-
γ	-	26.7 [64.5]	26.8, 26.6	26.9 [65.4]	26.2 [100.6]	-
δ	-	13.4	13.5	13.5	13.4	-

[a] In $CDCl_3$, coupling constants $^nJ(^{119}Sn,^{13}C)$ in Hertz are given in [ ].
[b] ^{13}C NMR chemical shifts for $R^1 = CH_2CH_2SCH_3$ in compound **(6)**, 28.5,31.2,15.2 ppm.
[c] Compound **(3)** is distannoxane.
[d] Numbering scheme for carbon atoms is as follows:



R = Me **(1)**, **(6)**, Bu **(2)**, **(3)** R = Bu **(4)**, **(5)**

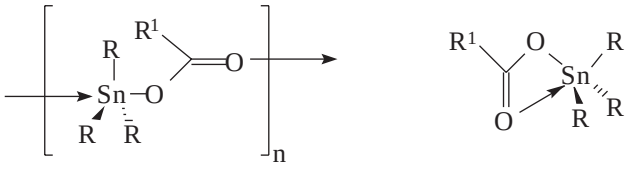
R^1 = H, $CH_2CH_2SCH_3$

a
SnR = Sn-CH_3

a b g d
SnR = Sn-$CH_2CH_2CH_2CH_3$

^{119}Sn NMR is also a powerful technique for the determination of the coordination number of tin [8]. Generally triorganotin carboxylates, $R_3SnOCOR^1$, are known to adopt a variety of motifs in the solid state [4,5,9,10]. This includes 5 coordinated tin polymeric structures **A** and less often 5 coordinated tin monomeric structure **C**. However, in solution, such structures appear as 4-coordinated, the additional coordination from the carbonyl oxygen to tin being lost [10]. In similar fashion the δ ^{119}Sn chemical shifts of compounds **(1)**, **(2)**, **(4)** and **(6)** are comparable with earlier reports describing tetrahedral geometry [8,10]. A difference of more than 250 ppm in the ^{119}Sn chemical shift for compound **(5)** compared with triorganotin carboxylates suggests a coordination number greater than 5 for tin [10]. Dicarboxylatotetraorganodistannoxane dimers of the type $\{R^1COO(R_2Sn)\text{-}O\text{-}(SnR_2)OOCR^1\}_2$ are easily characterized in solution by standard NMR techniques as their solution structure gives rise to 2 ^{119}Sn resonances of almost equal intensities, appearing in the ^{119}Sn chemical shift range –170 to –230 ppm and exhibiting $^2J(^{119}Sn\text{-}O\text{-}^{119/117}Sn)$ coupling satellites [10,26]. Compound **(3)** exhibits the 2 ^{119}Sn NMR resonances of almost equal intensities characteristic for

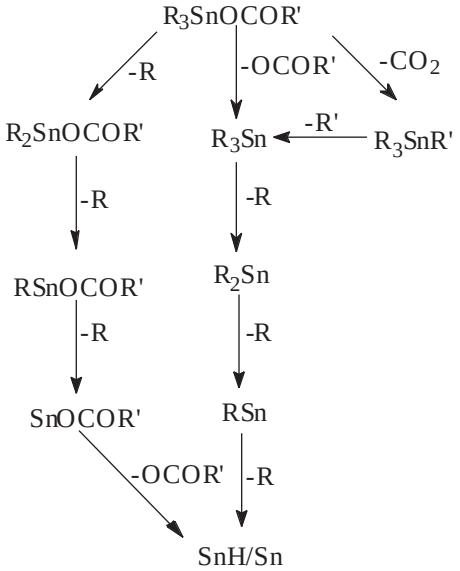
the 5-coordinated endocyclic and exocyclic tin atoms of the dimeric dicarboxylatotetraorganodistannoxane structure as shown in Figure 1 (Scheme 4).



A **C**

Table 3. C-Sn-C angles (°) based on NMR data.

Comp. No. ↓	$^{2}J(^{119}Sn,^{1}H)$	$^{1}J(^{119}Sn,^{13}C)$	$\theta(°)$	
			^{2}J	^{1}J
(1)	61.0	424.0	112.4	112.3
(2)	–	350.6	–	109.8
(4)	–	355.9	–	110.3
(5)	–	567.0	–	131.4
(6)	59.6	402.0	111.5	112.0

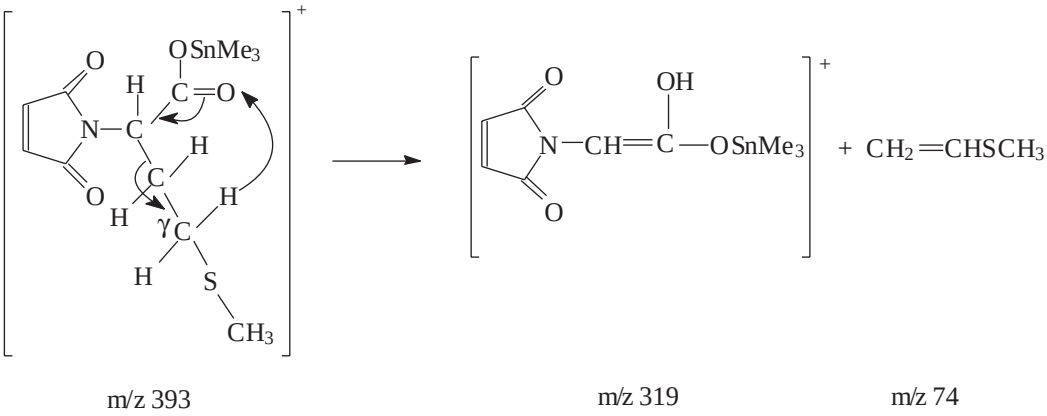


Scheme 5

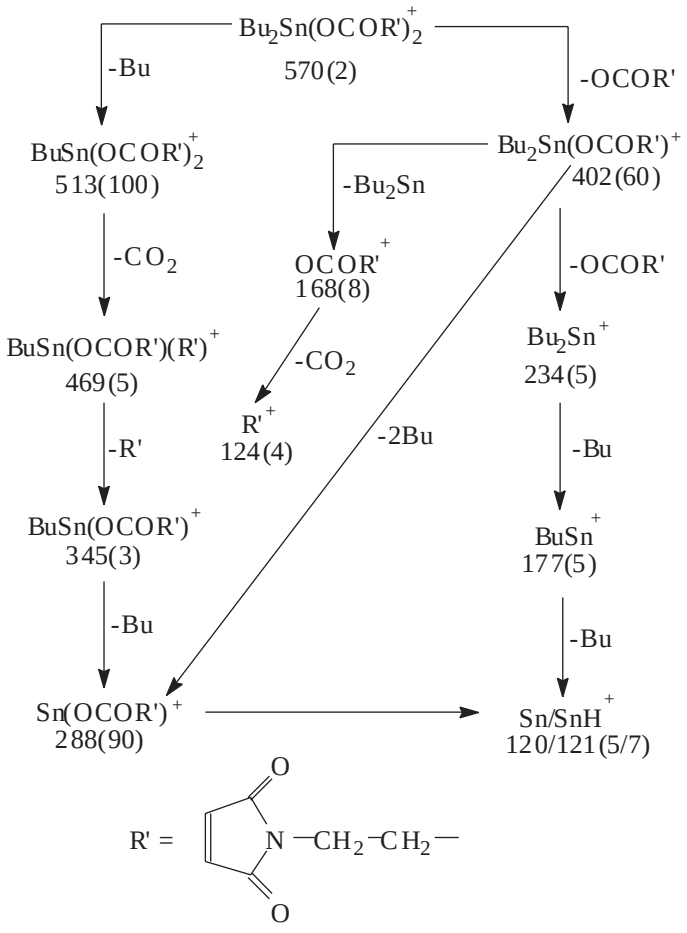
Mass spectrometry

The major conventional EI mass spectral data of compounds **(1-6)** are given along their synthesis in the experimental section. Since each fragment ion occurs as a group of peaks as a result of tin isotopes, only the mass spectral data presented here are related to the principal isotopes, namely ^{120}Sn. Scheme 5 represents the general fragmentation pattern based on the loss of different groups from the parent molecule ion for the triorganotin compounds. This general scheme is in good agreement with analogous compounds reported elsewhere [40−42]. One interesting feature is the observation of McLafferty rearrangement in the mass spectrum of compound **(6)**, as shown in Scheme 6 [43]. The compound **(6)** fulfills the requirement for this rearrangement,

i.e. the presence of γH (γ-hydrogen). Scheme 7 shows the possible fragmentation pathway for compound **(5)**. A similar pattern is observed for compound **(3)**. A reasonably good compatibility is found between the suggested and published fragmentation pathways [32].



Scheme 6

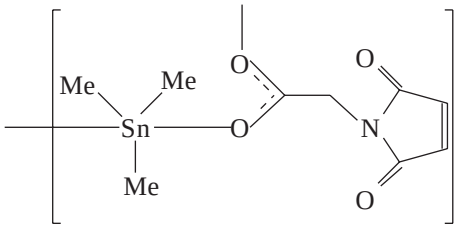


Scheme 7

Main features of X-Ray analysis

Compound **(1)** [19]

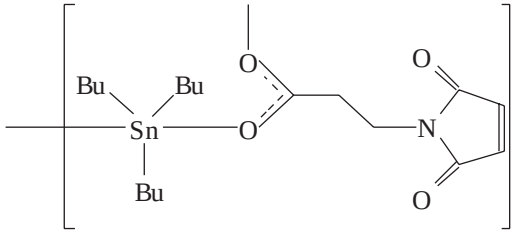
monoclinic, space group $P2_1/c$ ($a = 6.585(15)$, $b = 9.991(4)$, $c = 19.688(4)$ Å, $\beta = 93.31(3)°$, $Z = 4$, $D_{calc} = 1.633$, $R = 0.041$, $wR(F^2) = 0.147$, $S = 1.202$)



(1)

Compound **(4)**[20]

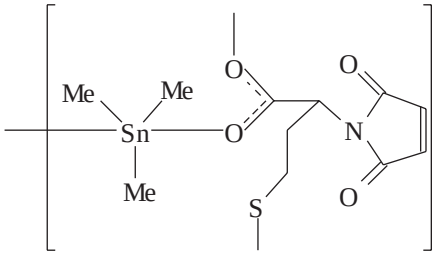
monoclinic, space group $P2_1/a$ ($a = 10.574(3)$, $b = 16.812(2)$, $c = 12.882(2)$ Å, $\beta = 102.15(2)°$, $Z = 4$, $D_{calc} = 1.359$, $R = 0.039$, $wR(F^2) = 0.141$, $S = 1.020$)



(4)

Compound **(6)** [21]

monoclinic, space group $P2_1/n$ ($a = 6.507(5)$, $b = 9.640(3)$, $c = 26.376(3)$ Å, $\beta = 91.51(3)°$, $Z = 4$, $D_{calc} = 1.574$, $R = 0.059$, $R_w(F^2) = 0.159$, $S = 1.224$)



(6)

The structures of compounds **(1)**, **(4)** and **(6)** contain polymeric chains wherein each trialkyltin moiety bridges 2 neighboring N-maleoylamino acids via carboxyl groups. The Sn atom has distorted trigonal bipyramidal geometry, with 3 alkyl groups in the equatorial plane. The carboxyl O atoms bonded to the Sn atom in the axial positions have significantly different Sn-O bond lengths (2.207(5) and 2.358(6) Å for

compound **(1)**, 2.215(5) and 2.424(5) Å for compound **(4)**, 2.152(6) and 2.484(6) Å for compound **(6)**). The molecular dimensions in all the ligands are normal.

Conclusions

Six organotin(IV) carboxylates with N-maleoyl amino acids were prepared by 2 different methods and characterized by various spectroscopic techniques. The coordination mode of ligands with tin was determined by FT-IR. The solution and solid-state chemistry of the synthesized compounds was discussed in term of multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) and ^{119m}Sn Mössbauer spectroscopy. Different fragmentation patterns were proposed on the basis of mass spectroscopy. McLafferty rearrangement was observed in compound **(6)**.

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